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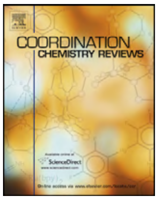

Review

Recent developments in the field of metal complexes containing photochromic ligands: Modulation of linear and nonlinear optical properties

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ABSTRACT

Organic photochromic molecules are important for the design of photoresponsive functional materials, as switches and memories. Over the past 10 years, research efforts have been directed towards the incorporation of photoresponsive molecules into metal systems, in order either to modulate the photochromic properties, or to photoregulate the redox, optical and magnetic properties of the organometallic moieties. This review article focuses on some of the recent work reported within the last few years in the area of organometallic and coordination complexes containing photochromic ligands for the photoregulation of optical and nonlinear optical properties. The first part is related to photochromic 1,2-diarylethene (DAE)-containing metal complexes, examples of mono- and multi-DAE metal-based will be discussed. The second part deals with metal complexes incorporating spiropyran and spirooxazine derivatives.

1. Introduction

Photochromism, which refers to the reversible color change of a compound with light irradiation, is attracting much attention for the construction of molecular devices. During the past decade, there has been a growing interest in the synthesis, properties and applications of organic photochromic materials [1–7]. Photochromic materials have been the focus of intensive investigations from both the fundamental and practical points of view for their potential applications to optically rewritable data storage, optical switching, and chemical sensing. Useful properties that may be photoregulated include luminescence, refractive index, electronic conductance, magnetism, optical rotation, nonlinear optics, redox chemistry. Photochromic transformations are generally based on unimolecular processes involving the interconversion of two isomers, such as *cis*/*trans* isomerization, ring opening/closing or intramolecular proton transfer. So far, various types of organic photochromic compounds such as azobenzenes, diarylethenes, fulgides, spirobenzopyrans, dimethyldihydropyrenes have been developed. Metal complexes featuring photoresponsive ligands are an interesting alternative to pure organic photochromes. Combining a photochromic moiety with an organometallic or coordination compound provides new properties deriving from the combination of redox, optical and magnetic properties of the metal complexes with the photochromic reaction.

The scope of this review is to discuss some of the recent work made in the area of photochromic organometallic and coordination compounds which are used for the photomodulation of luminescence and nonlinear optical (NLO) properties. Reversible changes of

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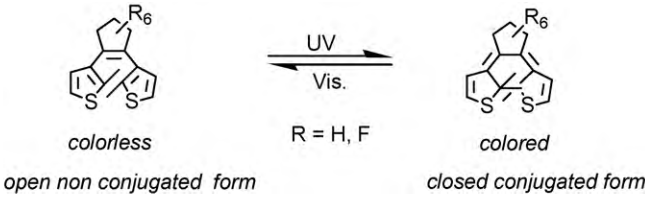
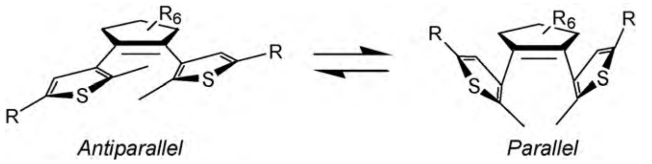


Scheme 1. Photochromic interconversion of a dithienylethene (DTE) unit.



Scheme 2. Parallel and anti-parallel conformations of DTE.

luminescence are interesting from the viewpoint of applications for erasable memory media, optical switches and luminescent probes, and switchable NLO molecules are potentially useful for the development of molecular photonic devices. This review concentrates on selected recent examples of metal complexes featuring two types of photochromic units, the diarylethenes and the spiropyrans or spirooxazins, which have been attracting much interest for their photoswitching capabilities. Other known types of photochromic metal complexes based on azo compounds which have already been the scope of several reviews [8–10] will not be discussed here.

2. Photochromic diarylethene-containing metal complexes

Diarylethene (DAE) derivatives that have been used as ligands for incorporation into transition-metal complexes have recently received much attention. Coordination of DAE ligands opens up new perspectives for the design of photoswitchable molecules. Among the diarylethene family, 1,2-dithienylcyclopentene (DTE) and its perfluoro analogue have particularly attracted increased interest for their excellent stability and fatigue-resistance properties, not only in the solution but also in the single-crystalline phase [11–14]. Irradiation at appropriate wavelength allows the interconversion of a non-conjugated colorless *open* form to the conjugated, colored, *closed* form via a 6π electrocyclic reaction of the 1,3,5-hexatriene moiety in the molecule (Scheme 1) [3,15].

The open-ring isomer of DTE has parallel and anti-parallel conformations which are in dynamic equilibrium (Scheme 2). The closing process follows the rules according to Woodward–Hoffmann, in which the photocyclization occurs, via a conrotatory mechanism, only from an anti-parallel conformation of the two thienyl rings. For unsubstituted DTE derivatives, the ratio of molecules in the parallel and anti-parallel conformations is close to 1:1 and the cyclization quantum yield therefore cannot exceed 0.5. The photocycloreversion is significantly less efficient than the photocyclization, in most cases the quantum yield values typically not exceeding 0.1.

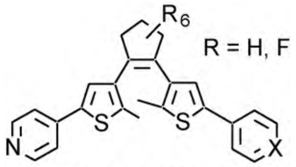
Upon photocyclization, the properties of the dithienylethene moiety change dramatically, resulting in a different photochemical, photophysical, and electrochemical behaviour of the open and closed forms.

2.1. Photophysical properties and photoregulation of luminescence

Among outputs, luminescence emission is considered to be one of the most attractive, owing to the ease of detection and the cheap fabrication of devices in which it is detected. Many examples of fluorescence photoregulation of photochromic molecules have been published by combining a DTE unit with an organic fluorophore [4]. Moreover, the access to triplet states by incorporation of the DTE fragment into the ligands of transition-metal complexes allows the photoregulation of phosphorescence.

2.1.1. Mono-DAE metal-based complexes

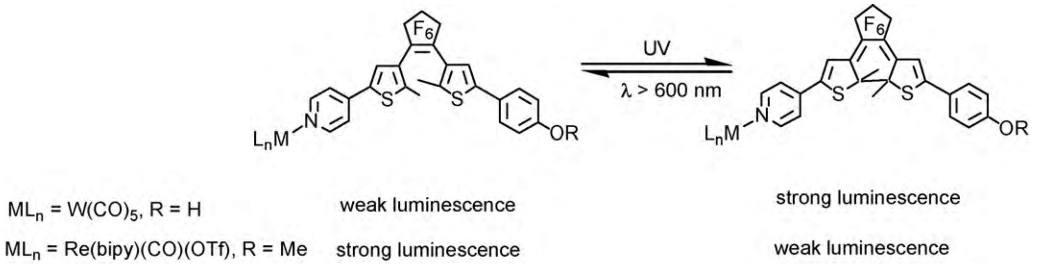
During the last decade, pyridine derivatives, such the *monodentate* 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene and the *bidentate* 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene, incorporating the DTE moiety as the photochromic unit (*4-py-DTE$_f$* [16–19] and *4-py$_2$-DTE$_f$* [20] and the non fluorinated analogue (*4-py$_2$-DTE*) [21] have been coordinated to various transition metals, allowing the change of physical properties of metal complexes.



4-py$_2$-DTE (X = N)
4-py-DTE (X = CH)

For example, Lehn developed the synthesis and luminescent properties of complexes of tungsten and rhenium of *4-py-DTE$_f$* and *4-py$_2$-DTE$_f$* (Scheme 3) [17,18]. The tungsten pentacarbonyl complexes were found to display a luminescence discrimination between the (weakly emissive) open and (strongly emissive) closed forms when excited at 240 nm, a wavelength of irradiation that almost did not affect the state of the molecule. The bipyridine rhenium(I) complexes also displayed a modulation of luminescence when excited in the same region, but in these cases the emission intensity was always stronger for the open form.

The photochromic properties of mono- and dinuclear transition-metal complexes containing DTE-conjugated bipyridine (*bipy-DTE-bipy*) and phenanthroline (*phen*) ligands have been investigated by several groups. De Cola reported homo- and hetero-dinuclear systems in which the metallic fragments $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ are bridged by a dithienylperfluorocyclopentene



Scheme 3.

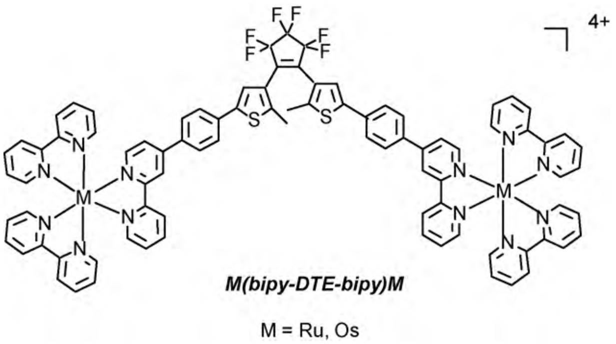


Fig. 1. Chemical structure of dinuclear transition-metal complexes containing DTE-conjugated bipyridine ligands.

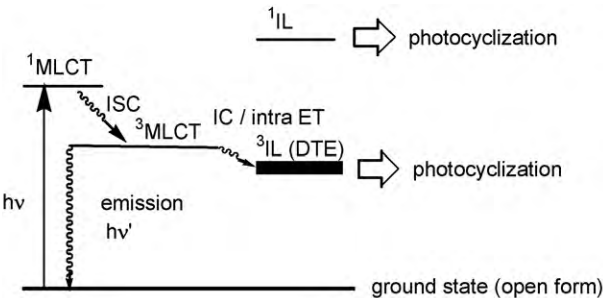


Fig. 3. Proposed qualitative energetic scheme for photosensitized photochromism by MLCT.

molecular switch, a phenylene group being used as a spacer (Fig. 1) [22–24].

The open form of the uncoordinated ligand *bipy-DTE-bipy* in acetonitrile is colorless (Fig. 2A). The absorption maximum at 321 nm corresponds to $S_0 \rightarrow S_1$ singlet intraligand (^{1}IL) transition localized on the photochromic unit while the shoulder at 285 nm involves the $\pi \rightarrow \pi^*$ transition of the free bipyridine ligand. Upon conversion to the closed form, the solution turns blue. The cyclization forces the system into a more planar conformation, thereby increasing the conjugation and lowering the energy of the $S_0 \rightarrow S_1$ (^{1}IL) transition of the photochromic unit which shifts from 321 to 605 nm.

The electron-withdrawing metal center induces a lowering of the lowest unoccupied molecular orbital (LUMO) on the photochromic unit, resulting in a shift of the corresponding absorption band to a significantly lower energy compared to the free ligand (Fig. 2B). The $S_0 \rightarrow S_1$ (^{1}IL) transition band of the photochromic unit is found at 345 nm in the bimetallic system *Ru*(*bipy-DTE-bipy*)*Ru*. On going from the open to the closed form, the new absorption band grows at 614 nm, ascribed to the ^{1}IL transition of the cyclized dithienylethene unit.

In these metal systems, De Cola demonstrated that the photochromism can be extended from the UV region in the free ligand to the visible region corresponding to the metal to ligand charge transfer (MLCT) transition. The extension of the excitation wavelengths to the visible region to trigger the photochromic reaction allows the use of less destructive visible-light sources and is highly desirable. Direct evidence of triplet MLCT (^{3}MLCT) photosensibilization of the ring-closing reaction of diarylethene has been reported by means of transient absorption and time-resolved emission studies. The ring-closure reaction is in the nanosecond domain and the quantum yield decreases strongly in the presence of dioxygen. The photosensitization mechanism involving an internal conversion or intramolecular energy transfer from the ^{3}MLCT state to the triplet intraligand ^{3}IL(DTE) state has been demonstrated. Once the singlet MLCT (^{1}MLCT) state is populated, intersystem crossing (ISC) to the ^{3}MLCT state would occur leading to the sensitization of the photochromic reactive ^{3}IL(DTE) state that initiates the ring-closure reaction (Fig. 3). This behaviour differs substantially from the photocyclization process of the non-emissive DTE free ligand, which occurs from the lowest ^{1}IL state on the picosecond timescale and is insensitive to oxygen quenching. Replacement of both Ru(II) centers by Os(II) completely prevents the photocyclization reaction upon light excitation into the lowest-lying ^{1}MLCT excited state.

A disadvantage of such system is that, in the trapping state, energy is transferred to the photochromic moiety that can consequently convert to the parent form. Therefore, monitoring the occurrence or absence of energy transfer cannot be used as means for non-destructive readout, as the excitation affects the state of the system. The possible quenching by the sensitized photocyclization renders the photoluminescence from the ^{3}MLCT state less efficient. Upon conversion to their respective closed form, the ^{3}MLCT emission of both Ru(II) and Os(II) complexes are quenched. This is due to an energy transfer to the lowest excited state of the DTE unit that is lower in energy than those of the metal centers in the closed form.

The parent hetero-dinuclear Ru/Os complex was also investigated. The bridging unit in its open form allows an efficient energy transfer from the excited ruthenium to the acceptor osmium center. When the bridging DTE unit is in its closed form, the energy level IL(*closed*-DTE) drops down and is below of the energy level of the two metal centers, quenching both emissions.

Yam reported the synthesis and sensitized photochromic properties of a versatile diarylethene-containing 1,10-phenanthroline ligand *phen1* (Fig. 4) and its metal complexes (Re [25,26] and Pt [27]). Unlike other studies where the ligand is covalently connected to the DTE unit, *phen1* displays an original design in which the ligand itself is part of the dithienyl framework.

Unlike most other DTE systems, in which rapid interconversion of the two conformers results in a time-average ^{1}H NMR signals,

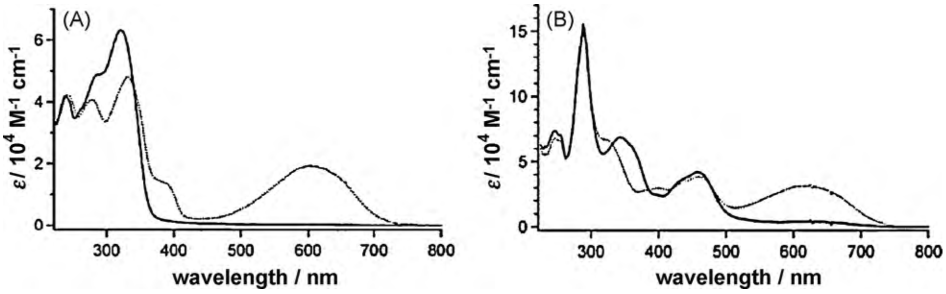


Fig. 2. (A) UV–vis absorption spectra of *bipy-DTE-bipy*(*o*) (black line) and a solution of *bipy-DTE-bipy*(*o*)/*bipy-DTE-bipy*(*c*) at the photostationary state (plotted line). The latter spectrum corresponds to a 98% photoconversion of *open* to *close bipy-DTE-bipy* in CH_3CN solution (293 K). (B) UV–vis absorption spectra of Ru(*bipy-DTE-bipy*)*Ru*(*o*) (black line) and a solution of the photostationary state (plotted line). The latter spectrum corresponds to a 97% photoconversion of *open* to *closed* Ru(*bipy-DTE-bipy*)*Ru* in CH_3CN solution (293 K). Reprinted with permission from [22]. ©(2004) American Chemical Society.

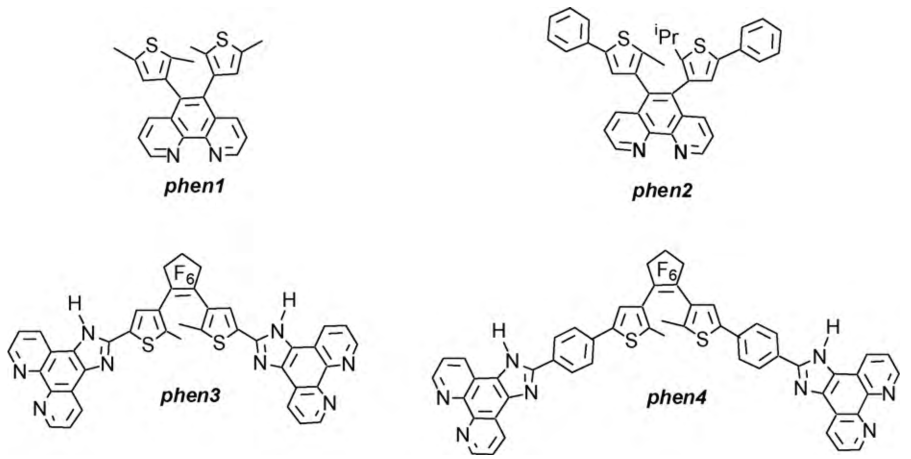


Fig. 4. Chemical structure of DTE-containing 1,10-phenanthroline derivatives.

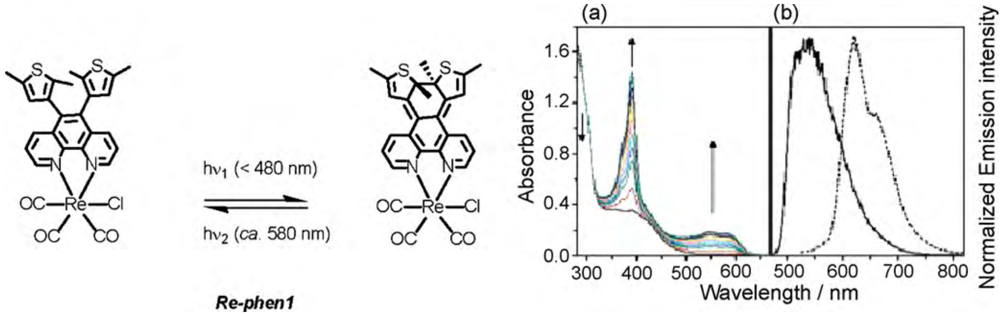


Fig. 5. (a) UV–vis absorption spectral changes of *Re-phen1* in benzene (7.16×10^{-5} M) upon MLCT excitation at 440 nm. (b) Overlaid normalized corrected emission spectra of the open (black line) and the closed (plotted line) forms of *Re-phen1* in EtOH–MeOH glass (4:1, v/v) at 77 K. Reprinted with permission from [25]. ©(2004) American Chemical Society.

the protons at the 4- and 7-positions of the sterically demanding phenanthroline moiety hinders the rotation of the thienyl rings. Thus, the parallel and anti-parallel conformations of the free ligand *phen1* and the rhenium complex *Re-phen1* (Fig. 5), are distinguished by the presence of two-well-resolved sets of ^{1}H NMR signals. The structure of the free ligand *phen1* shows that two thiophene rings tend to orient themselves perpendicular to the plane of the phenanthroline moiety.

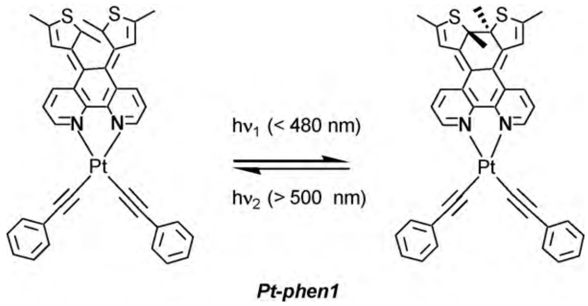
Insights into the mechanism of the photochromic reactivity were provided by ultrafast transient absorption and time-resolved emission spectroscopy. Direct evidence for the photosensitization of the cyclization by the ^{3}MLCT excited state of the rhenium, involving the ^{3}IL state of the DTE-containing ligand, has been demonstrated for the first time.

The ligand *phen1* has been also used to prepare the bis(alkynyl)platinum complex *Pt-phen1* (Scheme 4). The structure of the two conformers, parallel and anti-parallel, has been resolved. This is the first example of X-ray crystal structures in which both isomers of the same photochromic molecule have been determined.

In these systems, no quenching of luminescence is observed, since the DTE unit is part of the phenanthroline ligand. Perturbation of the photochromic and luminescence properties upon coordination to the metal center (Re, Pt) has been observed. A red shift of the absorption band for the closed isomer is attributed to the perturbation of the metal center in the complex (Fig. 5). The emission of both *phen1*(*o*) and *M-phen1*(*o*) (MLCT) (*o*: open form; *c*: closed form) changes upon conversion to the closed form in the photostationary state (PSS). The strong red shift of the emission observed for the closed form *phen1*(*c*) is attributed to the extension of the π-conjugation and has an IL ($\pi \rightarrow \pi^*$) phosphorescence in origin. A close resemblance of the emission of *M-phen1*(*c*) with that of *phen1*(*c*) suggests that the IL excited state, lower-lying in energy than that of the MLCT excited state, is the predominant emissive state.

Unlike the symmetrically substituted analogue *phen1*, the unsymmetrically substituted DTE-containing 1,10-phenanthroline ligand *phen2* (Fig. 4) and the corresponding *Ru-phen2* (Fig. 6) exhibit no photochromic properties [28]. The diarylethene-containing imidazo[4,5-*f*][1,10]phenanthrolines *phen3* and *phen4* (Fig. 4) have been synthesized but no examples of metal complexes reported yet [29]. These ligands are sensitive to both light (UV/visible-light irradiation) and chemical stimuli (alkali/acid treatment). A reversible four-state molecular switch has been realized by a single molecule.

The study of a 1,2-bis(2-methylbenzothiophen-3-yl)maleimide model (*phen-DAE*) and two dyads in which the photochromic unit is coupled via a direct nitrogen-carbon bond (*Ru-phen-DAE*) or through an intervening methylene group (*Ru-phen-CH$_2$-DAE*) to a Ru-polypyridine chromophore (Fig. 6) has provided strong evi-



Scheme 4.

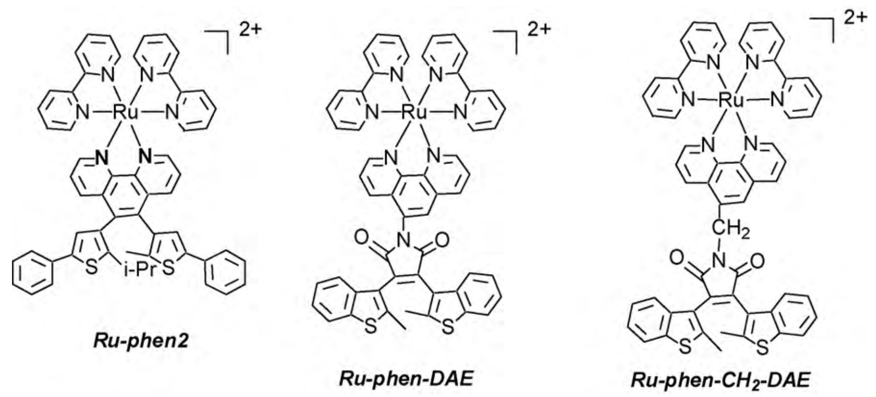
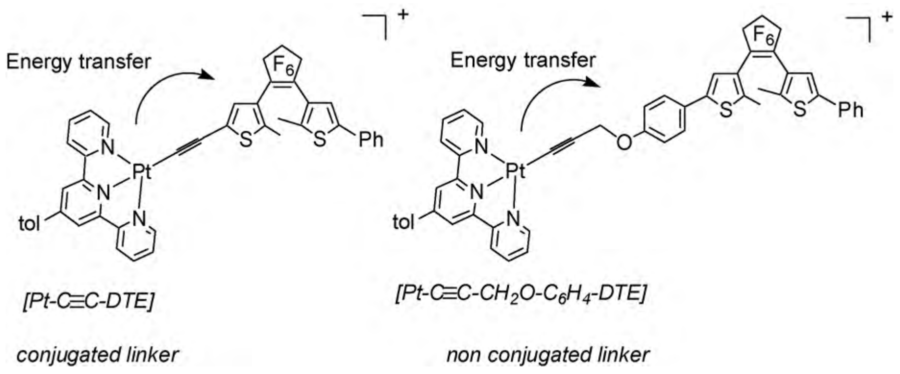


Fig. 6. Chemical structure of ruthenium complexes containing photochromic 1,10-phenanthroline derivatives.



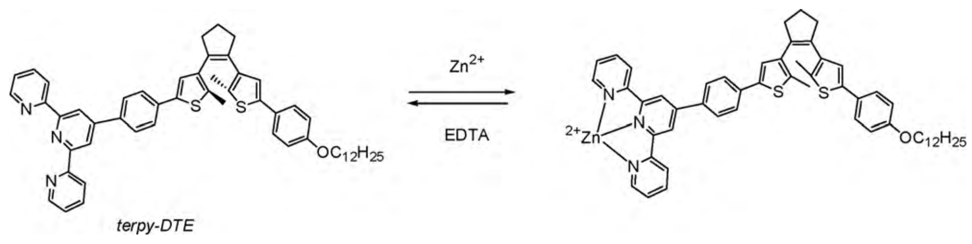
Scheme 5.

dence for the participation of triplet state in the photochromic behaviour of this class of diarylethenes [30]. Unlike previous studies, evidence of triplet reactivity case is obtained not only for the metal-containing systems but also for the isolated *phen-DAE*. A complete kinetic characterization has been obtained by ps–ns time-resolved spectroscopy. The experimental results were complemented by a combined *ab initio* and density functional theory (DFT) computational study whereby the potential energy surfaces for ground state and lowest triplet state of the DAE are investigated along the reaction coordinate for photocyclization/cycloreversion.

The metal-sensitized ring closing of dithienylethene can depend on the nature of the linker group between the organometallic moiety and the photochromic unit. This role has been recently investigated by Branda and Wolf in the case of (terpyridyl)platinum-DTE complexes containing two types of alkynyl linkers (Scheme 5) [31].

As for the above-mentioned examples, ring closing of the complex [*Pt–C≡C–DTE*] can be triggered directly by irradiation with UV light which is absorbed by the DTE chromophore, or indirectly by selective excitation of the MLCT/LLCT absorption bands of the metal complex component with visible light. In the case of a longer non π-conjugated linker between the metal and the DTE moieties as in [*Pt–C≡C–CH$_2$–OC$_6$H$_4$–DTE*] the cyclization process cannot be triggered with broad-band ($\lambda > 415$ nm) irradiation into the MLCT/LLCT band. This shows the necessity for the two components to be linked in a particular fashion for energy transfer to occur between ^{3}MLCT/LLCT and ^{3}IL states. Emission from complex [*Pt–C≡C–CH$_2$–OC$_6$H$_4$–DTE*] is characteristic of platinum terpyridyl ^{3}MLCT-based phosphorescence.

Tao Yi has designed and synthesized an amphiphilic diarylethene *terpyDTE* as a photoswitchable probe for imaging living cells, by combining diarylethene and terpyridine units (Scheme 6) [32]. The compound *terpyDTE* exhibits several clearly different and reversible fluorescence states that can be controlled by varying light frequency and metal ion concentration. As expected, *terpyDTE* shows reversible absorption and fluorescence intensity changes with the alternate irradiation with UV and visible light. In addition, the fluorescence intensity can be reversibly controlled by Zn/ethylenediaminetetracetic acid (EDTA): Zn^{2+} acts as a trigger for fluorescence switch-OFF while EDTA acts as a trigger for fluorescence switch-ON.



Scheme 6.

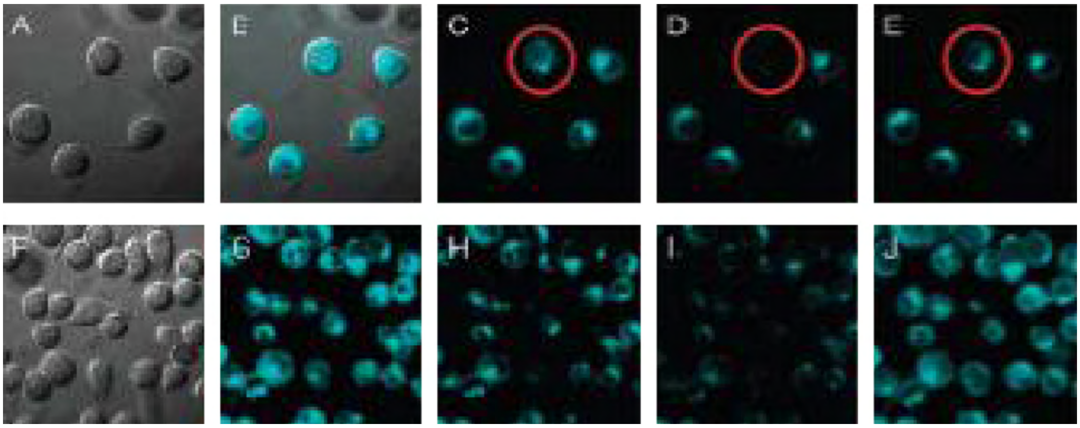
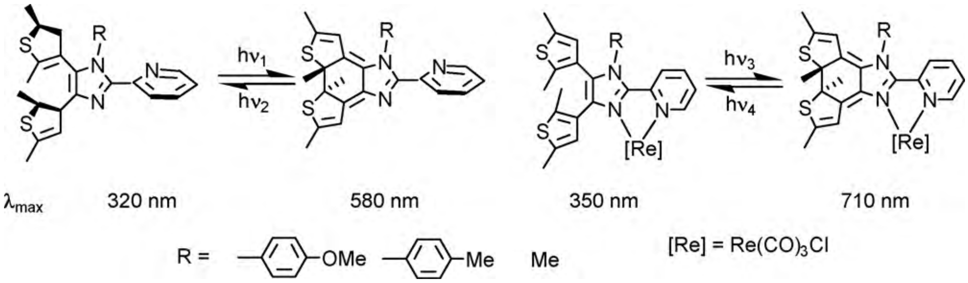


Fig. 7. Confocal laser scanning microscopy (CLSM) images of KB cells incubated with *terpyDTE* for 20 min at 25 °C (1×10^{-5} M in PBS/DMSO, 100:2, v/v). (A and F) Brightfield transmission image of KB cells. (B) Overlay image of A and C. Confocal fluorescence image of (C) original state, (D) irradiated by 405 nm light (2 mW, 3 min) for one selected cell and (E) recovered by 633 nm light (0.7 mW, 40 min). Confocal fluorescence image of (G) original state of F, and incubation by Zn^{2+} solution with the concentrations of (H) 5×10^{-5} M, (I) 1×10^{-4} M. (J) Recovered by 5×10^{-4} M EDTA solution. Reprinted with permission from [32]. ©(2009) American Chemical Society.



Scheme 7. Photochromic behaviour of DTE-containing 1-aryl-2-(2-pyridyl)imidazole ligands and their Re(I) complexes.

Having low cytotoxicity, *terpyDTE* can enter live cells as a fluorescence probe and can act as a detector for the biological process of the metal ion transmembrane transport (Fig. 7).

Metal coordination of the DTE derivative and extension of the π-conjugated system through an enhancement of planarity provides an alternative and versatile route to a new class of photochromic compounds that show absorption and reactivity in the near-infrared (NIR) region. The Re(I) complexes featuring a DTE-containing 1-aryl-2-(2-pyridyl)imidazole ligand has been demonstrated to exhibit NIR photochromic behaviour, with a large red shift in absorption maxima upon photocyclization that has been brought by metal coordination-assisted planarization of the extended π-conjugated system (Scheme 7) [33]. In the open forms of the uncoordinated ligands, the pyridyl and imidazoyl rings are twisted with respect to each other and are not coplanar. Upon photocyclization, only the imidazoyl and the two thienyl rings are locked into a coplanar conformation, leading to a bathochromic shift of the IL(*closed*-DTE) band. On the contrary, coordination to the Re(I) metal center would force the 2,2′-linked pyridyl and imidazoyl ring into co-planarity from the twisted conformation, causing an increase in the extent π-conjugation. The emission intensity of open forms of the Re complexes ($R = C_6H_4$-OMe, C_6H_4-Me) decreased when photocylization took place.

2.1.2. Multi-DAE metal-based complexes

A few examples of metal complexes containing several DTE units have been reported. Generally, like their organic congeners [34–36], the conversion to the fully closed isomer is not observed, this is attributed to intramolecular transfer from the reactive state (open part) to the closed-ring DTE part, the lower-lying excited state. Park and co-workers developed a novel class of heteroleptic cyclometalated Ir(III) complexes covalently linked to one and two DTE switches (Fig. 8) in order to study the phosphorescence modulation. Upon irradiation with UV light, the mono DTE complexes

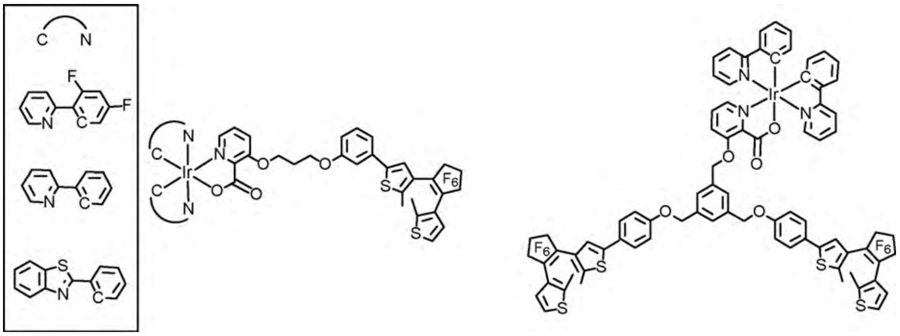
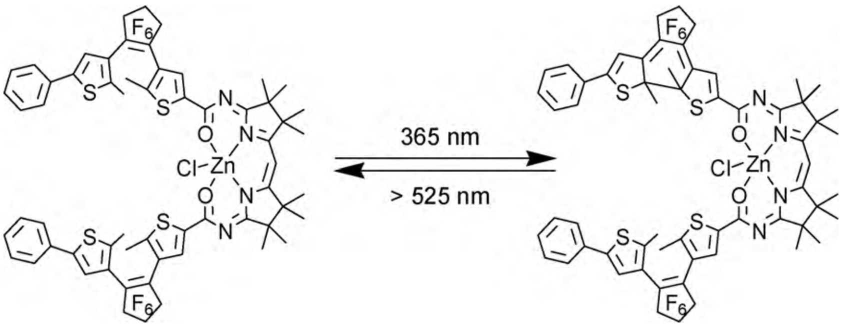


Fig. 8. Chemical structures of cyclometalated Ir(III) complexes covalently linked to one and two DTE switches.



Scheme 8.

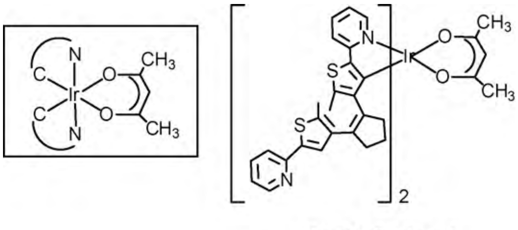


Fig. 9. Chemical structure of the cyclometalated (*py-BTE*)$_2$*Ir*(*acac*).

were converted to the corresponding closed isomers (67–90% conv. at PSS), whereas the bis-DTE complex afforded mainly at the PSS a photoproduct in which one of the two DTE units is in its closed form (90% conv.). All the open form isomers were moderately phosphorescent when excited with 355 nm light. On the other hand, a significant reduced emission was observed upon conversion to the photostationary states, the best phosphorescence modulation being achieved with the bis-DTE iridium complexes (Φ_p on/off ratio ≈ 10). In these systems, the phosphorescence modulation is likely due to energy transfer occurring from the Ir(III) complex to the closed form DTE unit [37].

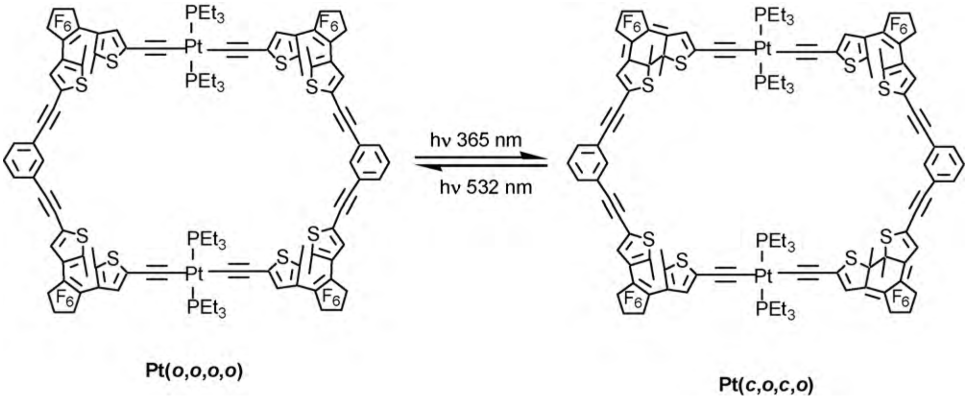
A second example of a photochromic Ir complex has been published by Tian [38] in which the thiophene ring of the DTE fragment is directly linked to the metal center (Fig. 9). Complex (*py-BTE*)$_2$*Ir*(*acac*) showed excellent near-infrared photochromic behaviour accompanied by efficient quenching of phosphorescence emission.

Branda also described a system that combines the highly fluorescent zinc bis(acylamidine) with two photochromic DTE units (Scheme 8) [39]. Again in this system, only one dithienylethene unit underwent cyclization upon UV light. Upon UV excitation, the fluorescence of the system was quenched due to efficient intramolecular energy transfer although photoinduced electron transfer cannot be ruled out. The fluorescence was also quenched in thin films, but, according to the authors, the decrease of the photoresponse may be due to the lack of flexibility to convert non-productive parallel conformation to the productive anti-parallel one.

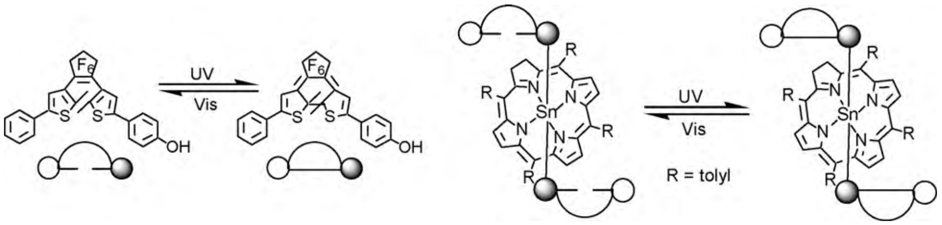
Ko and co-workers reported the synthesis and photochromic properties of a Pt macrocycle Pt(*o*,*o*,*o*,*o*) containing four dithienylethene units (Scheme 9). Upon UV irradiation, only two photoinduced cyclization reactions occurred, giving rise to the closed-ring isomer Pt(*c*,*o*,*c*,*o*) (88% conv. at PSS). The high value of the cyclization quantum yield (0.64) was attributed to the enforced anti-parallel conformation in the macrocycle [40].

An europium(III) complex having two photochromic *terthiazole* ligands has been synthesized by the Kawai group in order to realize reversible control of Ln^{III} luminescence (Fig. 10). The luminescence of the Eu(III) complex *Eu*(*THIA*)$_2$(*HFA*)$_3$ (*THIA*: 4,5-bis(5-methyl-2-phenylthiazole) was efficiently quenched when the photochromic ligand THIA was converted from the colorless ring-open form to the closed-ring form upon UV light irradiation, resulting in a modulation of the emission intensity of 70% at 614 nm [41]. The quenching effect was attributed to the energy transfer from the $^5D_0$ excited state to the ligand in the closed-ring form.

Very recently Yam et al. have incorporated diarylethene moieties into the core of imidazolium salts with the goals to generate ionic liquids and novel NHC complexes with photoswitchable functional properties, such as switchable catalytic, regio-, or enantioselective activities (Fig. 11) [42]. A series of DTE-containing imidazolium salts and the NHC complexes of Au(I), Ag(I), Pd(II) have been synthesized. Similar to other compounds with two DTE moieties, the photocyclization of the second moiety in the bis(DTE-NHC)-based Au complex was not observed, as the result of the quenching effect of the first ring-closed moiety. The open forms



Scheme 9.



Scheme 10.

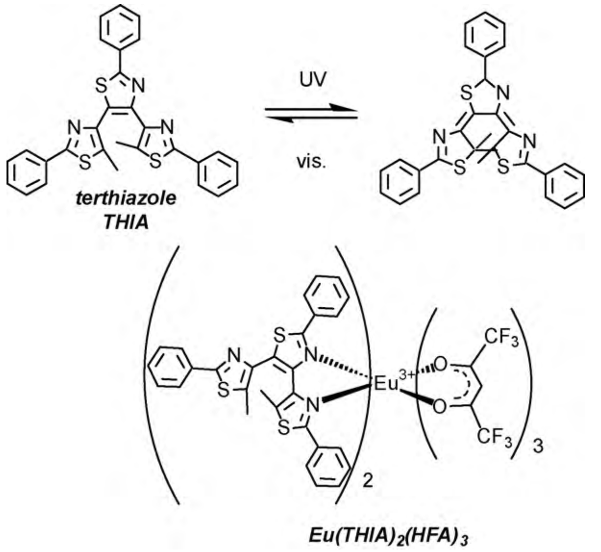


Fig. 10. Chemical structure of an Eu(III) complex containing two photochromic terthiazole ligands.

of all compounds (except the Au(DTE-NHC)(carbazole) complex) were non-emissive whereas the closed forms display an emission into the red, tentatively assigned as metal-perturbed IL of the condensed thiophene units, probably with some mixing IL(carbene character).

The preferential coordination of the tin(IV) porphyrins to oxy anionic ligands has been used for the elaboration of the photochromic fluorophore Sn(TTP)(DTE-Ph-O)$_2$ (TTP: 5,10,15,20-tetratolylporphyrinato) in which two phenolic derivatives of DTE (DTE-Ph-O) are axially coordinated in *trans* position (Scheme 10). Unlike the above examples, it was suggested that upon UV irradiation the photochromic isomerization of the two DTE units occurred simultaneously without any transient species on the time scale of UV–vis absorption spectroscopy (63% conv. at PSS). In the open form the porphyrin exhibited high fluorescence intensity at 609 and 664 nm when excited at 410 nm. Small changes of the fluorescence intensity (about 16%) in the luminescence modulation were observed in the photostationary state [43].

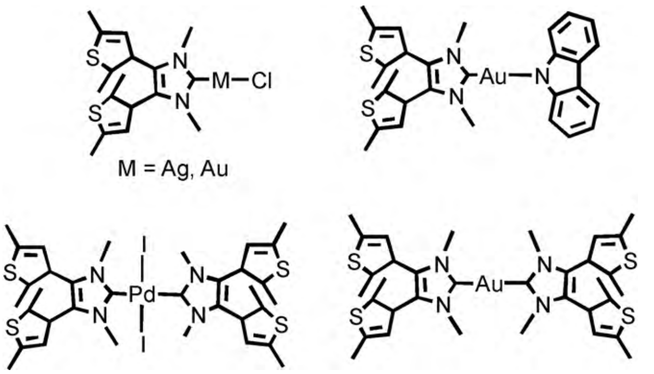
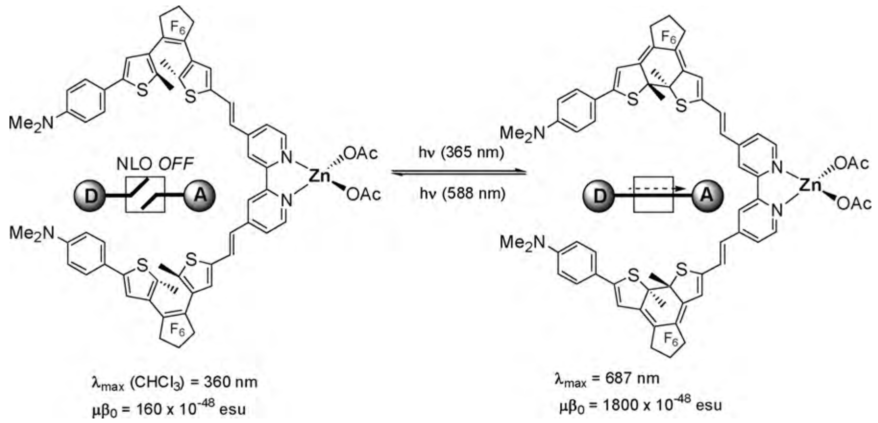


Fig. 11. Chemical structure of photochromic NHC complexes of Au(I), Ag(I), Pd(II).

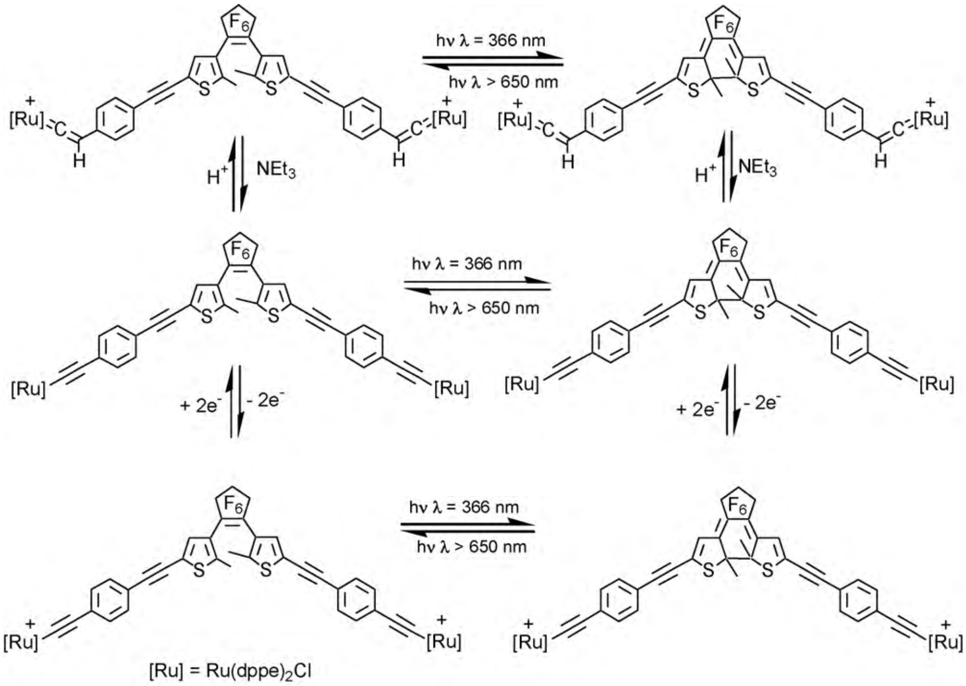
2.2. Switching optical nonlinearities of metal complexes

A current challenge is the development of efficient strategies for the design of switchable nonlinear optical (NLO) materials. The ability to switch "ON/OFF" the NLO activity of a molecule is of relevance for the development of molecular photonic devices those properties can be switched by modifying one of the component parts [44,45]. To achieve an efficient switching effect, the molecule must be stable in the two ON and OFF states and the response time must be relatively fast. As most molecules with large quadratic hyperpolarizability values comprise π-systems end-capped with donor and acceptor moieties, various strategies have been proposed and categorized into three types [44]. The first two types include the alteration of either the electron-donor or the electron-acceptor capacity of the end groups by using external stimuli such as redox and protonation/deprotonation. The third type includes the alteration of the π-bridge using an external trigger such as light, and in this category photochromic compounds seem to be promising candidates for the design of photoswitchable NLO materials [46–48]. Donor-substituted styryl bipyridine metal complexes [49–51] are push–pull NLO chromophores, and modulation of the NLO properties of has been achieved by varying the donor terminal group as well as metal center [52]. In order to carry out the photoswitching of the NLO properties, a new type of 4,4′-bis(ethenyl)-2,2′-bipyridine ligands functionalized by a dimethylaminophenyl–dithienylethene (DTE) group and the corresponding zinc(II) complex have recently been designed by Le Bozec. This molecule undergoes an efficient reversible interconversion between a non-conjugated open form and a π-conjugated closed form when irradiated at 365 and 588 nm, respectively (Scheme 11). The NLO properties have been evaluated by Electric Field Induced Second Harmonic Generation (EFISH) measurement for the open and PSS closed forms: the $\mu\beta_0$ value for the open form is very small, in agreement with the absence of π-conjugation between the two thiophene rings of the DTE fragment. Upon conversion to the closed form in the photostationary state, the NLO activity dramatically increased, from 160 to 1800 × 10^{-48} esu. Thus, the huge enhancement of $\mu\beta_0$ clearly reflects the efficient delocalization of the π-electron system in the closed form and demonstrates an efficient ON/OFF switching of the NLO responses.

Electron transfer is an appealing process allowing the same transformation as in photochemistry, i.e. cyclization-reopening of diarylethenes. In this context, the DTE unit has proven to be useful for the elaboration of photo and/or electrochromic metal-based systems specially devoted to the control of the electronic communication in bimetallic complexes [53–59]. For example, a binuclear metal alkynyl complex incorporating the ruthenium carbon-rich fragments [Ru(dppe)$_2$(Cl)(C≡C)] (dppe = 1,2-bis(diphenylphosphino)ethane) and a DTE bridge has shown to give rise to an efficient light- and electro-triggered switch featuring multicolor electrochromism [60]. A related bimetallic ruthenium complex has been used for the switching of cubic NLO



Scheme 11. Photoswitching of the quadratic NLO response by using a photochromic metal complex.



Scheme 12. Switching the cubic NLO properties of a photochromic ruthenium complex across six states.

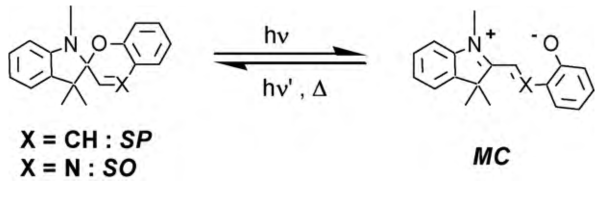
properties across six states [61]. The six states were interconverted along seven pathways, all of which resulted in distinct changes to cubic nonlinearity for specific region of the spectrum (Scheme 12).

3. Photochromic spiropyran and spirooxazine-containing metal complexes

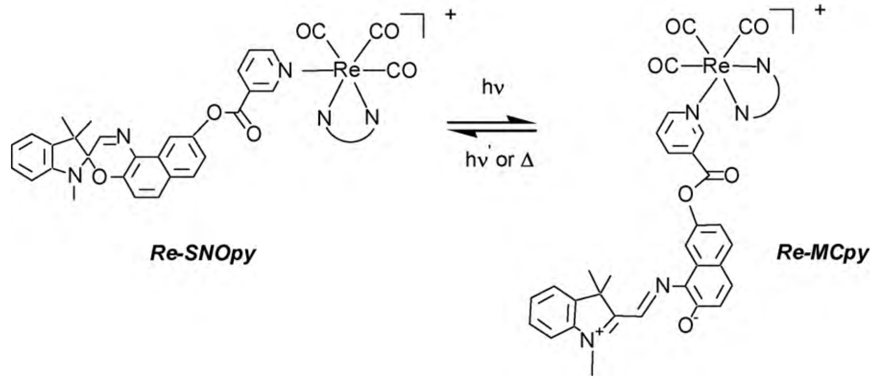
Spiropyrans (SP)/spirooxazines (SO) are another attractive class of photochromic molecules and have been extensively studied due to their fatigue resistance and good photostability [62,63]. The photochromic properties of spiropyrans were first recognized by Fischer and Hirshberg in 1952 [64]. The photochromism is attributed the photochemical cleavage of the spiro C–O bond, forcing the molecule to open up. This ring-opening reaction results in the extension of the π-conjugation in the colored photomerocyanine (MC) form which is thermally unstable and readily reverted by thermal reaction or by absorption of visible-light irradiation (Scheme 13). To date a few examples of transition-metal complexes incorporating a spiropyran or spirooxazine fragment into nitrogen-based ligands such as polypyridines and porphyrins have been developed and their photochromic and luminescent properties studied.

3.1. Spiropyran- and spirooxazine-containing polypyridine metal complexes

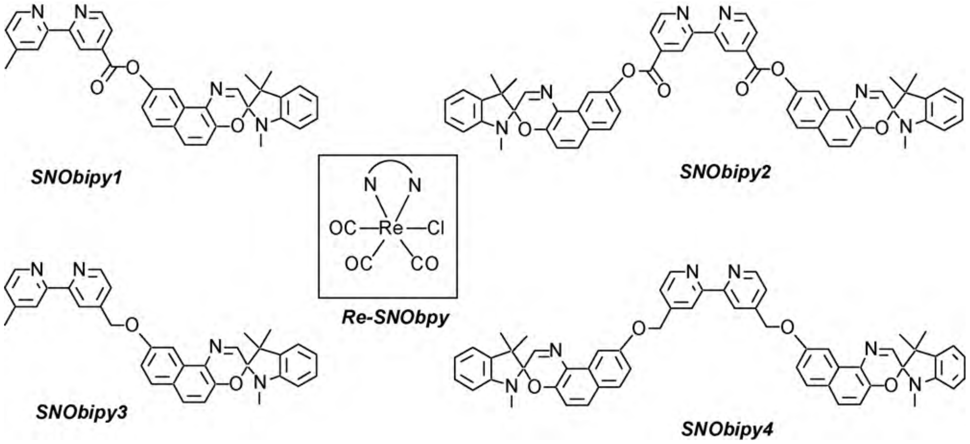
Spirooxazines (SO) are structurally and functionally very similar to spiropyrans. A series of rhenium complexes featuring a spironaphthoxazine-based pyridine ligand (*SNOpy*) $[Re(CO)_3(phen)(SNOpy)]^+$, $[Re(CO)_3(4,4'\text{-}Me_2\text{-}bipy)(SNOpy)]^+$, and $[Re(CO)_3(4,4'\text{-}^tBu_2\text{-}bipy)(SNOpy)]^+$ (*SNOpy*: 1,3,3-trimethyl-



Scheme 13. Photochromic interconversion of typical spiropyran and spirooxazine.



Scheme 14.



Scheme 15.

spiroindoline naphthoxazine-9′-ylnicotinate) have been synthesized and their photochromic behaviour demonstrated (Scheme 14) [65–67].

The *Re-SNOpy* complexes exhibit strong luminescence, the two emission bands are attributed to the ligand-centered (LC) fluorescence and phosphorescence. An assignment as MLCT phosphorescence was ruled out, since the emission energies are insensitive to the diimine ligands, irrespective of their different π* orbital energies. The formation of the photomerocyanine (*Re-MCpy*) open form upon MLCT excitation is suggestive of an efficient photosensitization of *Re-SNOpy* by the MLCT excited state. It is likely that an intramolecular energy transfer from ^{3}MLCT to the *SNOpy* moiety occurs, to give the ^{3}SNOpy state, which would either return back to the ground state with emission of light or undergo the ring-opening process to give the colored *Re-MCpy* form.

The *Re-MCpy* form is thermally unstable and readily undergoes thermal bleaching which follows first order kinetics to the closed form. The decoloration rate constant of the *Re-MCpy* form strongly depends on temperature and on the nature of the solvent used, the zwitterionic *Re-MCpy* form being more stabilized in polar solvent such as MeOH. This constant decreases, in a small extent, upon addition of $ZnCl_2$, this could be attributed to the stabilization of the Re-MCpy form by the formation a Zn^{2+} complex [65].

The related 2,2′-bipyridine derivatives (Scheme 15) have been prepared and incorporated in Re complexes [Re(CO)$_3$(Cl)(*N,N-SNObipy*)] [66]. Their X-ray crystal structures reveal an orthogonal arrangement of the indoline and naphthoxazine planes (interplanar angle 88°2) and a relatively longer spiro C–O bond (1.47 Å), these features are commonly observed in related systems. Unlike the Re-*SNOpy* complexes [Re(bipy)(CO)$_3$(*SNOpy*)]$^+$, Re-*SNObipy* complexes do not exhibit any photochromism with MLCT excitation. This is probably because the energies of the ^{3}MLCT excited state of the complexes estimated from the phosphorescence of the complexes (~166–188 kJ mol^{-1}) are insufficient for the sensitization when compared to the triplet excitation states of spironaphthoxazines (~210–225 kJ mol^{-1}). The switching of their emission properties (^{3}MLCT to ^{3}LC phosphorescence of the merocyanine moiety) upon conversion to the open form has been reported.

The kinetics for the bleaching process (Re-*SNObipy* to Re-*MCbipy*) have been determined for both the free ligands and the complexes (Fig. 12).

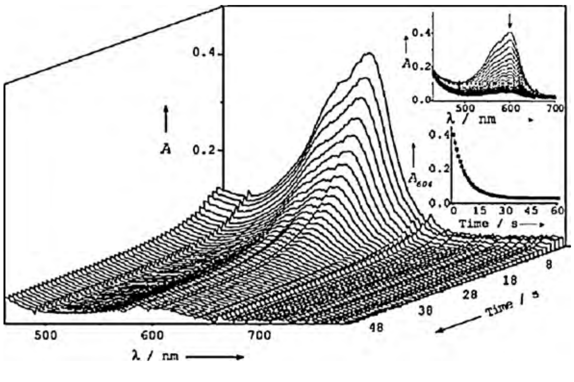
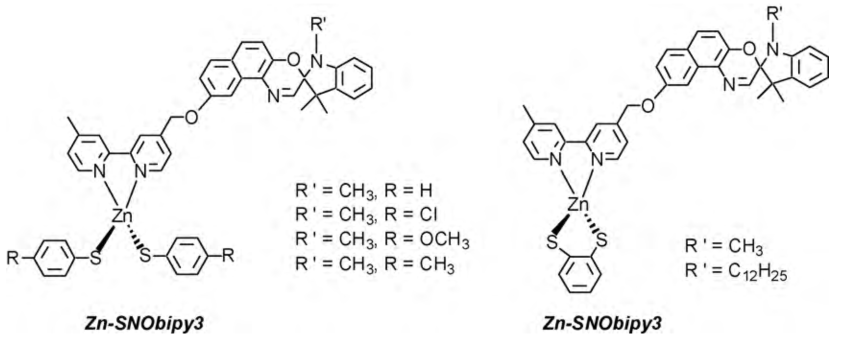
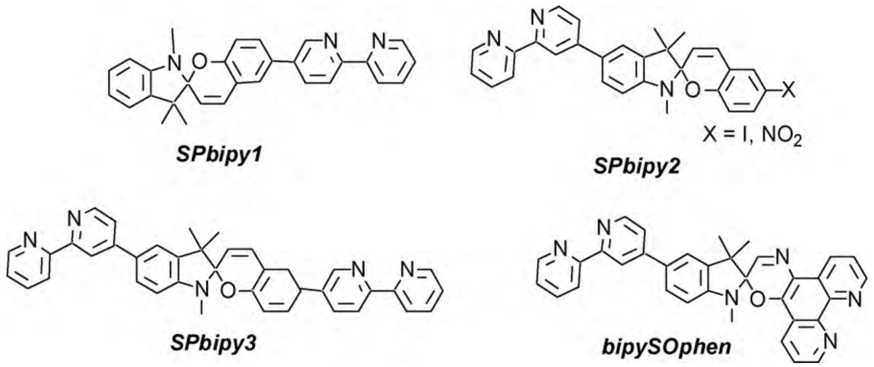


Fig. 12. Time-dependent UV–vis absorption spectral changes in the open form of Re(CO)$_3$(Cl)(SObpy$_4$) in acetonitrile after excitation at 365 nm. The inserts show the overlaid UV–vis absorption spectra at different decay times and the decay trace at the absorption maximum at 604 nm with time. Reprinted with permission from [66]. ©(2004) Wiley–VCH.



Scheme 16.

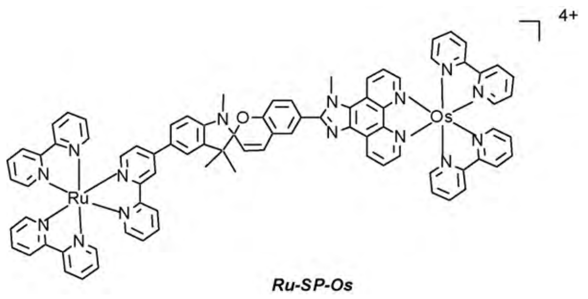


Scheme 17.

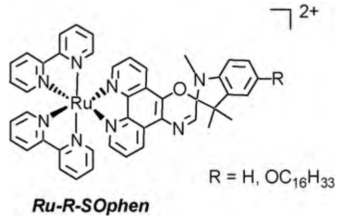
By incorporating these *SNObipy* ligands into various metal complex systems, their photochromic properties can be tuned and perturbed without the need of tedious synthetic procedures for the organic framework. As an extension of her work, Yam investigated a series of substituted spironaphthoxazine containing 2,2′-bipyridine and their Zn complexes bis-thiolate (Scheme 16) [67]. Upon excitation at 330 nm, all the ligands and complexes exhibit photochromic behaviour.

Spiropyran or spirooxazine units have been also bounded to 2,2′-bipyridine and 1,10-phenantroline: (i) the bipyridine moiety has been attached either to the pyran part (*SPbipy1*) or the indoline part (*SPbipy2*) of the spiropyran skeleton, (ii) the bipyridine ligand *SPbipy3* bears a bipyridine at each end of the spiropyran skeleton, (iii) a phenanthroline-based spirooxazine attached to a bipyridine ligand (*bipySOphen*) (Scheme 17) [68].

The photophysical, photochemical and redox properties of mononuclear complexes [M(bipy)$_2$(*NO$_2$-SPbipy*)]$^{2+}$ (M = Ru, Os) has been investigated (Scheme 18) [69]. These metallated nitrospiropyran compounds undergo efficient electrochemically induced conversion to the merocyanine open form, by first reducing the closed form and subsequently reoxidizing the corresponding radical anion in two-well-resolved anodic steps. Metal complexation of the spiropyran results in a strongly decreased efficiency of the ring-opening process as a result of energy transfer from the reactive excited spiropyran to the MLCT excited state. The lowest excited triplet state of the spiropyran in its open *MC* form is lower in energy than the excited triplet MLCT level of [Ru(bipy)$_3$]$^{2+}$ moiety but higher in energy than for [Os(bipy)$_3$]$^{2+}$, resulting in energy transfer from the excited ruthenium center to the spiropyran but inversely in the osmium case. However, the heterobinuclear complex *Ru–SP–Os* was shown to be inactive, no conversion to the open form occurred whatever the irradiation wavelength used (UV or visible (450 nm) light) [23].

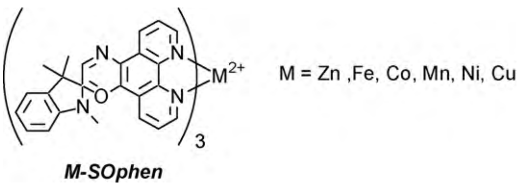


Scheme 18.

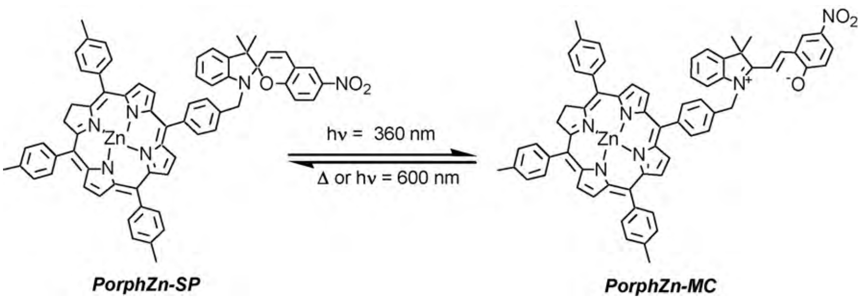


Scheme 19.

A dramatic increase in the ring-closing rate was observed for the *Ru–R–SOphen* (R = H, $C_{16}H_{33}$) complexes (Scheme 19), the effect



Scheme 20.



Scheme 21.

being attributed to the strong electron-donation ($d_\pi Ru \rightarrow \pi^*(N,N)$) of the $[Ru(bipy)_2]^{2+}$ fragment [70].

A series of M^{II}tris(spiro[indolinephenanthrolinoxazine]) (Mn, Fe, Co, Ni, Cu, Zn) have been synthesized (Scheme 20), resulting in tunable and significantly increased photoresponsivities (photocolorabilities) [71]. A significant stabilization of the photomerocyanine form results from metal complexation. An increase in charge density in the oxazine of the molecule leads to destabilization of the MC form. Metal complexation is expected to decrease the negative charge density of the oxazine moiety through inductive effects and to increase the charge density through $d_\pi M \rightarrow \pi^*(N,N)$ donation. The increase in photomerocyanine stability suggests that inductive effects play a dominant role.

3.2. Porphyrin-spiropyran metal complexes

Bahr et al. have developed a new dyad by linking a photochromic nitrospiropyran moiety to a zinc porphyrin (PorphZn-SP) [72]. They showed typical photochromic behaviour, i.e. conversion to the open merocyanine form upon UV excitation which in turn closes to the spiro form thermally or by irradiation into its visible absorption band (Scheme 21). The emission properties of the two forms, *Porph*$_{Zn}$*-SP* and *Porph*$_{Zn}$*-MC*, were investigated. The fluorescence of the porphyrin is unperturbed by the attached spiropyran moiety in the closed form, whereas the porphyrin first excited singlet state is quenched by the merocyanine with a quantum yield of 0.93, reducing the lifetime from 1.8 ns to 130 ps. The quenching of luminescence was assigned to a singlet–singlet energy transfer. Thus, this photoswitchable quenching phenomenon provides light-activated control of the porphyrin first excited states.

4. Conclusion

A number of systems, where photoresponsive molecules are used as ligands to form metal complexes, mono- or multimetallic, have been reported during the last decade. Such complexes exist for a wide range of metal centers (Cr, Mo, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, Cu, Ag, Au, Zn) and more recently lanthanides (Eu). This report shows that the photochromic properties could be readily tuned by changing the nature of the metal system without modifying the photochromic ligand. Thus, by a rational design of metal centers and/or ancillary ligands, photochromic behaviour can be controlled or modified. In addition, triplet reaction pathways have been demonstrated, allowing the extension of the excitation wavelengths to lower energies, which are less destructive. Finally, these metal systems allow the photomodulation of optical properties such as phosphorescence, quadratic and cubic nonlinear optics for which the presence of the organometallic fragment is crucial for the mentioned properties. These investigations have been initiated 10 years ago and this field still has to be explored.

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